

Tracking POPs in Global Air from the First 10 Years of the GAPS Network (2005 to 2014)

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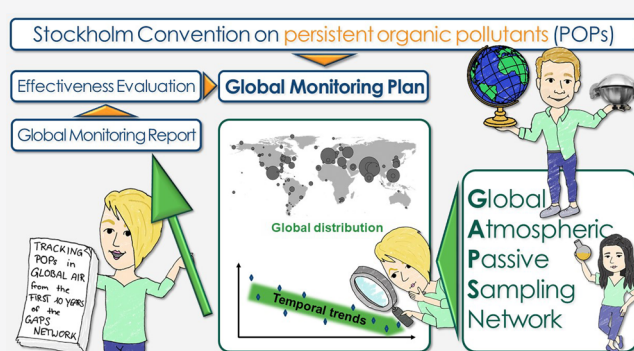
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ABSTRACT: The Global Atmospheric Passive Sampling (GAPS) network, initiated in 2005 across 55 global sites, supports the global monitoring plan (GMP) of the Stockholm Convention on Persistent Organic Pollutants (POPs) by providing information on POP concentrations in air on a global scale. These data inform assessments of the long-range transport potential of POPs and the effectiveness evaluation of chemical regulation efforts, by observing changes in concentrations over time. Currently, measurements spanning 5–10 sampling years are available for 40 sites from the GAPS Network. This study was the first time that POP concentrations in air were reported on a global scale for an extended time period and the first to evaluate worldwide trends with an internally consistent sample set. For consistency between sampling years, site- and sample specific sampling rates were calculated with a new, public online model, which accounts for the effects of wind speed variability. Concentrations for legacy POPs in air between 2005 and 2014 show different trends for different organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs). The POPs discussed in this study were chosen due to being the most frequently detected, with detection at the majority of sites. PCB, endosulfan, and hexachlorocyclohexane (HCH) concentrations in air are decreasing at most sites. The global trends reflect global sources and recycling of HCH, ongoing emissions from old stockpiles for PCBs, and recent use restrictions for endosulfan. These chlorinated OCPs continue to present exposure threat to humans and ecosystems worldwide. Concentrations of other OCPs, such as chlordanes, heptachlor and dieldrin, are steady and/or declining slowly at the majority of sites, reflecting a transition from primary to secondary sources (i.e., re-emission from reservoirs where these POPs have accumulated historically) which now control ambient air burdens.

KEYWORDS: *Global Atmospheric Passive Sampling network, persistent organic pollutants, temporal trends, effectiveness evaluation, global distribution*



INTRODUCTION

The Stockholm Convention on Persistent Organic Pollutants (POPs) is an international treaty that aims to eliminate or restrict the production and use of POPs. It listed an initial set of 12 chemicals when it was signed in 2001 and then ratified in 2004. The defining characteristics of POPs are persistence in the environment, adverse effects to human health and/or the environment, and the potential for long-range environmental transport and bioaccumulation.¹ Since ratification, 18 additional chemical groups have been added to the Convention (Figure S1). The mandate of the Stockholm Convention on POPs is to (a) eliminate dangerous POPs, (b) support the transition to safer alternatives, (c) target additional POPs for action, (d) cleanup old stockpiles and equipment containing POPs, and (e) work together for a POPs-free future.²

The effectiveness of the treaty is partially evaluated through the global monitoring plan (GMP) which compiles data from existing monitoring networks. The GMP also identifies data

gaps and supports strategies for establishing new monitoring programmes, developed by regional organizational groups. Information from the monitoring of the GMP core media air, water, and human tissues (milk and blood) is compiled to inform the effectiveness evaluation on a regular basis.^{1,3} The next regional reporting of the GMP will be presented to the Conference of the Parties in 2021 and will include the POP concentrations in air reported here for Global Atmospheric Passive Sampling (GAPS) years 2011 and 2014.

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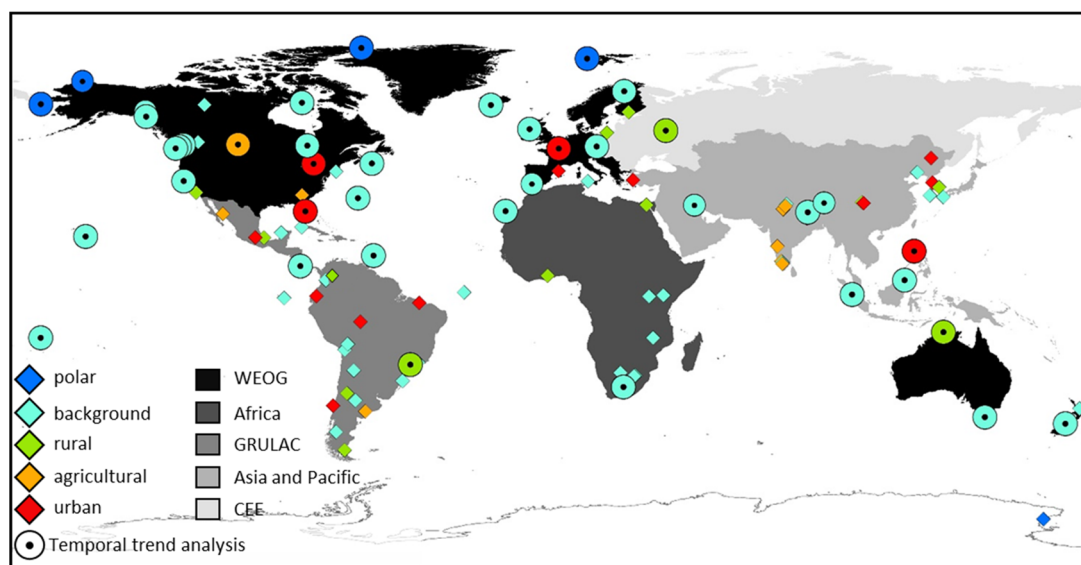


Figure 1. Map showing all 111 GAPS sites operated during 2005–2014, differentiated by usage and remoteness as polar, background, rural, agricultural and urban. 55 sites are currently still operational. The 40 sites with data available for 5–10 years are indicated (circle). The five UNEP working group regions are indicated using shading. WEOG – Western Europe and other Groups region; GRULAC – Group of Latin American and Caribbean Countries region, CEE – Central and Eastern Europe region, Africa and Asia and Pacific Group. Additional site information is presented in Figure S2 and the Supporting Information Excel file.

The GAPS Network has been in operation since 2005 to address monitoring needs for listed POPs in air for the global monitoring plan (GMP) under the Stockholm Convention and to provide new information (surveillance) on emerging chemicals of interest to support domestic (Canadian) and international risk assessment. Under the GAPS Network, passive air samplers (PAS), with polyurethane foam (PUF) disks as the sampling medium, are deployed for consecutive three-month periods at background, polar, rural, agricultural and urban sites. Data for legacy POPs monitored under the GAPS network is available for the deployment years 2005, 2006, 2007, 2009, 2011, and 2014. During these years, samples were deployed at 111 sites that are categorized as polar (PO, $n = 5$), background (BA, $n = 62$), rural (RU, $n = 17$), agricultural (AG, $n = 10$), and urban (UR, $n = 17$) (Figure 1, Figure S2). Due to the global coverage of the GAPS network, sites are located in all five United Nations Environmental Program (UNEP) Regional Groups, with 46 sites part of the Western European and Others Group (WEOG), 28 sites part of the Group of Latin America and Caribbean countries (GRULAC), 25 sites part of the Asia-Pacific Group, 9 sites part of the African Group, and 3 sites part of the Central and Eastern European Group (CEE). Long-term monitoring data covering 5–10 years is available for 40 of these sites.

The current study analyzed the global long-term monitoring data from the GAPS Network to determine temporal trends for a range of legacy POPs including polychlorinated biphenyls (PCBs), endosulfan and its degradation product endosulfan sulfate (SO_4), α - and γ -hexachlorocyclohexane (HCH), *cis*- and *trans*-chlordane, *trans*-nonachlor, heptachlor, heptachlor epoxide, and dieldrin. A new method to estimate local sampling rates, based on meteorological information, introduced by Herkert et al., was used to convert the new data and re-estimate previously reported POP data under the GAPS network to concentrations in air.^{4–6} The temporal trend analysis in this study was performed using the Theil-Sen Regression estimator. The accumulation of temporal trend data

from 40 sites on a global scale under one sampling campaign allows insight into regional differences that may be driven by historical use. Furthermore, compounds whose atmospheric levels are impacted by re-emission from secondary sources are identified through groupings based on the extensive temporal trend information.

EXPERIMENTAL (MATERIALS AND METHODS)

Sampling. The methodology for the sample preparation, extraction, and analysis are described in detail in previous publications.^{7–10} In short, precleaned polyurethane foam (PUF) disk samplers were deployed for three-month periods between the years 2005 and 2014 at 111 global sampling sites following the protocol of the GAPS network. Details for the deployment dates and sampling locations of the individual samples are reported in the Supporting Information (SI Excel-All data). The coefficient of variance for accumulated compound mass in duplicate PUF–PAS field samples was previously determined and reported as <35% by Gouin et al. (2005).¹¹

Sample Extraction, Analysis, and QA/QC. Samples were spiked with surrogate standards (¹³C-PCB-105, *d*₆- α -HCH, and *d*₈-*p,p'*-DDT) before extraction. Details on method recovery margins for 2005–2007 samples are reported previously,^{7,9,10} average recoveries for 2009–2014 were $95 \pm 30\%$. Samples for the years 2005–2007 were Soxhlet-extracted with petroleum ether.^{7–9} Samples for the years 2009–2014 were extracted with petroleum ether/acetone using accelerated solvent extraction (ASE 350, Dionex corporation, Sunnyvale, CA, USA).^{10,12} Extracts were concentrated using rotary evaporation and passed through an anhydrous sodium sulfate column. Extracts were analyzed for PCB 28/52/101/118/138/153/180 (reported as Σ_7 PCBs), endosulfan I/II/ SO_4 , α -/ γ -HCH, *cis*-/*trans*-chlordane, *trans*-nonachlor, heptachlor, heptachlor epoxide, and dieldrin using a Hewlett-Packard 6890 gas chromatograph–5973 mass spectrometer (GC-MS) for samples from 2005 to 2007 and an Agilent Technologies

Table 1. Geometric Mean Concentration of Legacy POPs at Different Site Types for GAPS 2011/2014^a

	Geometric mean concentrations in air between 2011-2014 [pg m ⁻³]					Halving/ <i>doubling</i> * time [years] (n = 40)
	Polar (n = 5)	Background (n = 62)	Rural (n = 17)	Agricultural (n = 10)	Urban (n = 17)	
Σ ₇ PCBs	10 ± 2.3	2.5 ± 4.5	4.8 ± 2.6	5.8 ± 1.8	27 ± 6.1	3.4
	2.2 - 78	0.013 - 97	0.76 - 53	2.1 - 14	1.0 - 320	2.3 - 11
α-HCH	36 ± 3.1	4.0 ± 4.8	2.2 ± 4.8	5.3 ± 3.4	3.5 ± 3.2	6.2
	1.5 - 210	0.07 - 106	0.26 - 150	0.83 - 39	0.079 - 19	4.4 - 170
γ-HCH	7.8 ± 2.4	3.2 ± 3.4	2.0 ± 3.7	4.9 ± 2.7	9.4 ± 3.7	9.7
	1.2 - 49	0.092 - 47	0.20 - 27	0.49 - 22	1.2 - 190	4.1 - 30
Endosulfan I	19 ± 2.4	12 ± 4.1	14 ± 4.1	96 ± 6.9	20 ± 5.2	3.0
	4.2 - 120	0.34 - 1200	1.6 - 360	9.3 - 2000	1.6 - 1600	2.1 - 4.6
Endosulfan II	2.1 ± 2.4	2.3 ± 7.1	3.4 ± 4.7	81 ± 7.5	7.6 ± 6.7	3.3
	1.2 - 6.5	0.05 - 220	0.22 - 88	1.2 - 710	0.085 - 280	1.6 - 6.7
Endosulfan SO ₄	0.16 ± 3.3	0.97 ± 0.010	1.9 ± 7.1	4.4 ± 14.1	1.6 ± 9.2	14
	0.069 - 0.38	0.0088 - 66	0.058 - 19	0.010 - 50	0.0098 - 120	5.0 - 27*
<i>cis</i> -Chlordane	2.6 ± 2.4	1.1 ± 3.3	3.6 ± 2.8	2.3 ± 2.6	7.6 ± 8.0	30
	0.37 - 9.8	0.0036 - 85	0.18 - 25	0.12 - 96	0.27 - 420	5.9 - 23*
<i>trans</i> -Chlordane	2.1 ± 2.9	0.79 ± 3.8	2.1 ± 5.0	1.9 ± 2.3	5.7 ± 12	17*
	0.39 - 16	0.034 - 26	0.077 - 15	0.29 - 5.6	0.090 - 400	15 - 7*
<i>trans</i> -Nonachlor	3.6 ± 2.2	1.6 ± 3.4	3.6 ± 3.4	2.9 ± 2.2	15 ± 5.3	7.1*
	0.55 - 14	0.016 - 17	0.12 - 21	0.51 - 8.2	0.92 - 240	58 - 4.9*
Heptachlor	0.11 ± 2.9	0.12 ± 4.7	0.73 ± 4.9	0.32 ± 2.8	2.2 ± 8.4	3.7
	0.031 - 0.56	0.0017 - 3.1	0.071 - 42	0.049 - 1.5	0.028 - 26	2.2 - 8.0
Heptachlor epoxide	2.9 ± 2.6	1.2 ± 3.5	1.9 ± 3.0	4.6 ± 3.3	2.8 ± 4.1	3.8
	0.26 - 12	0.037 - 12	0.28 - 14	0.47 - 28	0.13 - 26	2.9 - 5.8
Dieldrin	4.3 ± 2.0	3.1 ± 2.9	10 ± 3.9	11 ± 2.3	12 ± 4.4	5.2
	1.0 - 14	0.2 - 130	0.3 - 92	2.6 - 40	0.84 - 160	3.3 - 14

^a(Including geometric standard deviation, minimum and maximum) and the median halving/*doubling* times (including the range based on the 25th -75th percentile of temporal trend slopes). Doubling times are marked in **red** and with an * in the table.

(Mississauga, ON, Canada) 7890B gas chromatograph coupled with an Agilent 7000C tandem quadrupole mass spectrometer (GC-MS/MS) for samples from 2009 to 2014. Details on the GC-MS and GC-MS/MS methods are provided elsewhere.^{7,9,10} Updates in the extraction and analysis methods have undergone internal quality control to ensure the continuity of the results of the GAPS network.

Field blanks were deployed at all sites for all sampling years. Method detection limits (MDL) were estimated for each sampling year from the average concentration of the field blanks plus 3 times the standard deviation of the field blanks. All samples were blank corrected. The instrumental detection limit was used when all field blanks were nondetect for a compound. The complete data and sample specific MDL are reported in the SI-Excel Table "All data". As a result of improvements in instrument sensitivity over the past several years, MDL values have reduced substantially: by up to 1–2 orders of magnitude for some targeted chemicals. Consequently, this can introduce biases in the temporal trends assessment if MDL values are substituted (e.g., by 1/2 MDL), as discussed by Helsel et al.¹³ Therefore, the treatment of data under the GAPS Network for trends assessment is moving away from substitution (as was done in earlier papers, e.g., Pozo et al. 2006,⁹ Rauer et al. 2018¹⁰) and instead excludes data that fall below MDL, as was done in this paper. The MDL values are reported and flagged but not included in the temporal trends assessment. Other monitoring programs have also adopted this practice^{14–16} or apply more sophisticated approaches for substituting values below MDL (e.g., Monte Carlo methods) in order to reduce biases introduced by MDL substitution.^{17–19}

Geometric means (GM) and geometric standard deviation were calculated in Excel. Statistical tests suitable for the non-normally distributed GAPS data set were performed in R²⁰ using the packages "dplyr"²¹ and "openair".^{22,23} The Kruskal–Wallis Test was performed as a nonparametric alternative to the ANOVA test, coupled with the pairwise Wilcoxon Rank Sum Test as a nonparametric alternative to the *t* test. The package "pcaMethods"²⁴ was used to perform principle component analysis (PCA) with the "NIPALS" method for missing values.

Sampling Rates (R) and Concentration Conversion.

The mass loads per sampler were transformed to concentrations in air by using sample and compound specific effective air volumes. Previously reported concentrations in air from GAPS data were based on site-specific sampling rates (R) that were determined from depuration compounds (DC).⁹ Site-specific values in this study were estimated from the model and online tool by Herkert et al.^{4–6} The online tool estimates the modeled R values based on the GAPS depuration compound data and a meteorological model. The use of the online tool to estimate R values reduces sample processing steps and eliminates the high costs associated with isotopically labeled chemical standards. The model has been used and validated in other passive air sampling campaigns by Zhao et al. 2020²⁵ and Bohlin-Nizzetto et al. 2020.²⁶ Concentrations in air reported in this study are estimated from modeled R values (data reported in previous studies for the years 2005–2009 were corrected based on the new R values). Effective air volumes were calculated with the modeled R values following the method described by Shoeib and Harner.²⁷ Details for this approach are in the Text S1 and Figure S3.

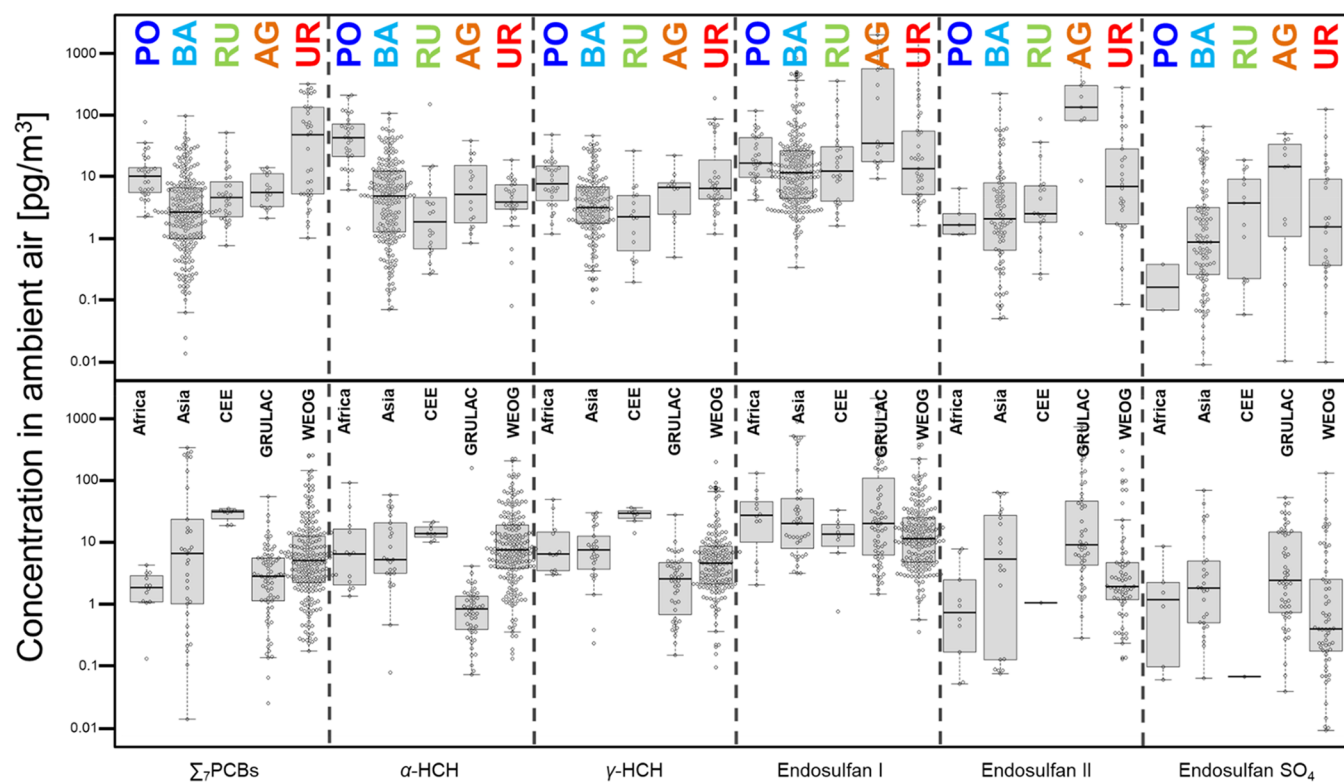


Figure 2. Global concentrations of Σ_7 PCB, α -HCH, γ -HCH, endosulfan I, endosulfan II, and endosulfan SO_4 for GAPS 2011/2014. The plot depicts the single data points using bee-swarm boxplots to illustrate the median, 25th and 75th percentile (whiskers marking the 10th and 90th percentile). The concentrations are resolved by sampling site type and UNEP regional group. (Site types: PO= polar, BA = background, RU = rural, AG = agricultural, UR = urban; UNEP regional groups: Africa = African Group, Asia = Asia and Pacific Group, CEE = Central and Eastern European Group, GRULAC = Group of Latin America and Caribbean countries, WEOG = Western European and Others Group).

Temporal Trend Analysis for the Data Set. Temporal trend analysis was performed for POPs (PCBs, endosulfan I/II/ SO_4 , α -/ γ -HCH, *cis*-/*trans*-chlordane, *trans*-nonachlor, heptachlor, heptachlor epoxide, and dieldrin) for 40 sites where data were available for a range of 5–10 years (Figure S1, Supporting Information Excel-Temporal trends). Dichlorodiphenyltrichloroethane (DDT) was excluded at this time due to analytical and detection challenges for its isomers and metabolites. The number of sites that fulfilled this condition were 4 polar, 28 background, 3 rural, 1 agricultural, and 4 urban sites. The Theil-Sen Regression estimator from the R package “openair” was used as a robust, nonparametric method to estimate the median regression slopes at individual sites and the overall global decline trend over the complete data set.^{22,23} The Theil-Sen Regression estimator has been used in other studies such as White et al. (2020) for the temporal trend analysis of POP levels in air from passive air sampling data.¹⁹ The Theil-Sen method estimates the slopes between all pairs of data points and returns the median of these slopes. The Theil-Sen Regression was only performed for sites with more than 6 data points (i.e., the natural logarithm of the POP concentration in air) above MDL. Data below the MDL were excluded from the statistical analysis. Details on the percentage of data used for the temporal trend analysis for each site and compound are reported in the SI (SI Excel-Temporal trends). First order kinetics was assumed to calculate the halving time or doubling time of POPs concentrations in the atmosphere from the slopes derived from the Theil-Sen Regression.

RESULTS AND DISCUSSION

Global Distribution of POPs Classes. The POPs discussed in this study were chosen due to being the most frequently detected, with detection at the majority of sites. The ranking of the detection frequency in 340 samples collected in the most recent GAPS years (2011 and 2014) is PCBs (97%, GM 4.0 ± 5.1 pg/m³) > endosulfan I (91%, GM 15.3 ± 4.4 pg/m³) > α -HCHs (83%, GM 4.8 ± 5.1 pg/m³) > dieldrin (76%, GM 4.5 ± 3.5 pg/m³) > *cis*-chlordane (72%, GM 1.9 ± 4.3 pg/m³) > γ -HCHs (69%, GM 4.1 ± 3.6 pg/m³) > *trans*-chlordane (60%, GM 1.4 ± 5.5 pg/m³) > *trans*-nonachlor (54%, GM 2.8 ± 4.2 pg/m³) > heptachlor epoxide (54%, GM 0.36 ± 7.7 pg/m³) > endosulfan SO_4 (43%, GM 1.2 ± 8.1 pg/m³) > endosulfan II (40%, GM 3.9 ± 8.0 pg/m³) > heptachlor (34%, GM 0.36 ± 7.7 pg/m³) (Table 1, Figure 2, Figures S4–S7). The variability in the detection frequency and concentrations reflect the history of use for the individual POPs in different areas.

PCBs are ubiquitous industrial pollutants which have been produced and in use since the 1930s. Production peaked in the 1960s, and the total global production is estimated at 1–1.5 million tonnes. Initial bans and regulations began in the 1970s, starting with the ban in Japan in 1972. The last official production ended in 1998. By the time PCBs were listed under the Stockholm Convention in 2004, they were restricted and banned globally. The applications of PCBs ranged from coolants and insulation fluids of transformers and capacitors; hydraulic fluid; lubricants; plasticizers in paint, cement, and copy paper; and additives in polyvinyl chloride, from electric cable coatings to sealants and caulking.²⁸ Their wide use means

that there is still an extensive number of remaining sources for PCBs in use and awaiting disposal. In addition to primary sources of PCB residuals, secondary sources for PCBs are believed to contribute to ambient air burdens by remission from environmental “sinks” where they have been accumulated over time (e.g., soils). This explains why they are the most ubiquitous POPs detected in this study. During the GAPS years 2011 and 2014, the highest concentrations were monitored at urban sites in the regional groups Asia and WEOG (Figure 2). This distribution pattern has not changed from the GAPS 2005–2007 data (Figure S4, S5).

Technical HCH was one of the most commonly used organochlorine insecticides after the 1940s. The technical mixture consisted of different HCH isomers with the most abundant being α -HCH (55–80%), β -HCH (5–14%), γ -HCH (8–15%), δ -HCH (2–16%), and ϵ -HCH (3–5%).²⁹ γ -HCH was identified as the only isomer that has specific insecticidal properties. Consequently, the use of technical HCH was discontinued in many countries during the 1950s and the product was replaced with lindane, which is the pure version of γ -HCH (99%). In some regions, like India and China, the switch to lindane came later, in the 1980s and 1990s. Lindane and the isomers α - and β -HCH were added to the list of restricted pollutants under the Stockholm Convention in 2009. Previous legislation focused mainly on the regulation of lindane, but the inclusion of the isomers α - and β -HCH emphasizes the need to address the global waste stockpiles of the lindane byproducts as well.

α -HCH was detected not only with higher frequency than γ -HCH in the GAPS 2011/2014 samples but also at overall higher concentrations at 60% of the sites. HCH concentration ranges were in general similar between polar, background, rural, and urban sites, with the exception of elevated α -HCH levels at polar sites. α -HCH was detected at higher levels at the polar sites in the Arctic compared to γ -HCH (Figure 2). This is also visible in the elevated fraction of α -HCH in polar samples ($82 \pm 9\%$) where both isomers were detected (Figure S8). The former Soviet Union was historically a source region for HCHs to the Arctic via long-range atmospheric transport.³⁰ Its consumption of technical HCH for agricultural use between 1950 and 1990 was substantially higher than lindane (total use of α -HCH ~ 1270 kt vs γ -HCH ~ 270 kt).^{30,31} The GAPS Network has not successfully established representative long-term sampling sites in Russia, which represents a large portion of the CEE region, to investigate levels and trends of HCHs and other POPs in air. Europe led in the overall consumption of lindane (63%) between 1950 and 2000 followed by Asia (16%) and North America (14%), while the use in Africa (6%) and Oceania (0.2%) was lower.^{32,33} This is reflected in overall higher concentrations of γ -HCH at European GAPS sites when compared to those of the other regions. There is a clear regional difference with α -HCH dominating concentrations in North-American WEOG sites (82%) compared to γ -HCH dominating concentrations at GRULAC sites (75%) (Figure 2). When comparing the average α - and γ -HCH patterns for GAPS 2011/2014 to GAPS 2005–2007, we find that concentrations in the Asia region were an order of magnitude higher than those in the other regions (Figure S4). We interpreted this difference as an artifact due to the termination of a large number of agricultural GAPS sites in the Asia region since 2007.

Endosulfan is an insecticide that is used as a technical mixture of the isomers endosulfan I and endosulfan II with

mostly agricultural application. The production as a commercial pesticide started in the 1950s, and it is estimated that the global consumption of endosulfan from 1950–2000 adds up to 308 kt.^{34,35} The highest consumption is reported for North America and parts of South America, Russia, India, and Australia.³⁶ Its use as a pesticide was banned in the European Union in 2006/2007 and it was listed under the Stockholm Convention on POPs in 2011, with exemptions. The endosulfan I fraction of both endosulfan isomers in the technical mixture is about 66–70%. Of the two isomers, endosulfan I is more stable. Endosulfan SO₄ is a major degradation product of endosulfan and is considered of toxicological concern. While endosulfan has higher environmental degradation rates than other POPs, endosulfan SO₄ is more stable and contributes to its joint persistence.³⁶ This is reflected by the higher detection frequency of endosulfan SO₄ compared to endosulfan II in this study, even though overall levels are about an order of magnitude lower than \sum endosulfan I/II levels. The highest endosulfan concentrations for GAPS 2011/2014 were observed at agricultural sites followed by urban > rural > background > polar sites (Figure 2). This is consistent with the distribution for GAPS 2005–2007 (Figure S4). The fraction of endosulfan I was calculated for all samples, where both endosulfan I and endosulfan II were detected. The endosulfan I fraction was higher than that in the technical endosulfan mixture (66–70%) for GAPS 2005–2007 ($83 \pm 12\%$) and GAPS 2011/2014 ($82 \pm 14\%$). The endosulfan I fraction decreases from polar sites > background > rural > urban/agricultural sites (Figure S9). The increasing endosulfan I fraction indicates an aging of the endosulfan mixture due to distance from source areas.

Dieldrin is an insecticide that was used for agricultural application and pest control. Commercial production of Dieldrin started in the late 1940s and peaked in the 1960s. In the 1950s, it was used extensively in the USA to target fire ants, but it had negative impacts on wildlife. The first restrictions of dieldrin started in the 1970s, but it was still in use in some countries until the 1990s.^{37–39} The range of monitored dieldrin levels in air is smaller compared to those of other compounds in this study (Table 1, Figure S6). We found no significant difference in concentrations between the UNEP regional groups. The concentration range for the site types was (highest to lowest) urban > rural/agricultural > background > polar (Figure S6). Dieldrin was predominantly used for pest control (i.e., wood treatment against termites, cloth treatment against moths), which is reflected in the highest detected levels at urban sites.

Chlordane and heptachlor are contact insecticides that were predominantly used for ant and termite control, landscaping, and limited agricultural applications since the 1950s. While chlordane and heptachlor were used globally, applications varied by regions. First restrictions and bans occurred in the 1980s.⁴⁰ Technical grade chlordane contains more than 140 compounds with composition of 24% *trans*-chlordane, 19% *cis*-chlordane, 21.5% chlordene isomers, 10% heptachlor, 7% nonachlor, and 16.5% other compounds.⁴¹ Heptachlor was released in the environment as a byproduct in the use of technical grade chlordane mixtures as well as a pesticide on its own.⁴² The heptachlor degradation product heptachlor epoxide is more stable in the environment.⁴³

The detection frequency and overall concentrations for *cis*-chlordane, *trans*-chlordane, and *trans*-nonachlor was higher than for heptachlor and heptachlor epoxide (Table 1, Figure

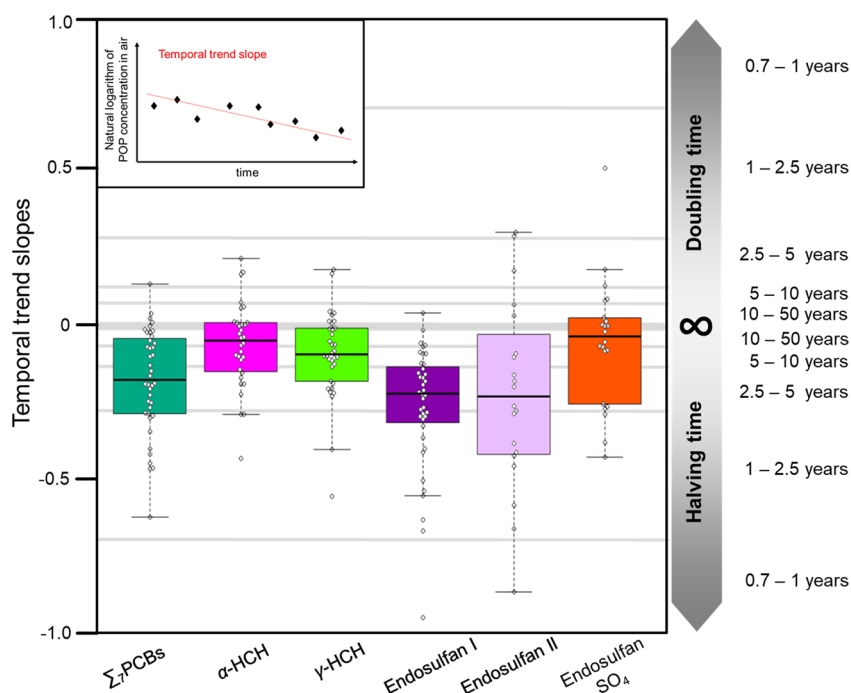


Figure 3. Temporal trend slopes for Σ_7 PCB, α -HCH, γ -HCH, endosulfan I, endosulfan II, and endosulfan SO_4 for GAPS 2005–2014. The temporal trend slopes were estimated with Theil-Sen regression for the 40 GAPS sites with sufficient data. The plot depicts the single data points and the boxplots marking the median, 25th and 75th percentile (whiskers marking the 10th and 90th percentile). The windows for halving/doubling times estimated from the temporal trend slopes following first order kinetics are marked in the graph.

S7). *cis*-chlordane, *trans*-chlordane, *trans*-nonachlor, and heptachlor show a similar distribution pattern across site types and regions with the highest concentrations in urban areas and in the Asia region. The technical chlordane mixture was used as treatment for structural wood and home lawn and garden in urban areas.⁴² The concentrations of the more stable degradation product heptachlor epoxide are not substantially different between site types and regional groups (Figure S7).

The focus of this paper is the reporting of trends and not the absolute concentrations of POPs or a comparison with other monitoring programs. An in depth compilation of POP concentrations on a global scale, which will include the GAPS data and data from other global programs, is forthcoming. Results for the 5 United Nations regional reports of the Global Monitoring Plan (third Phase) have been recently made available on the Stockholm Convention Web site,⁴⁴ and work on a unified global report will begin soon by an international expert group.

Temporal Trend Analysis. Temporal trend analysis was performed using the Theil-Sen method for 40 sites with sufficient data from 2005–2014 (Figure 1). The range of halving ($t_{1/2}$)/doubling (t_2) times was estimated based on the temporal trend slopes following first order kinetics. The 25th–75th percentile range for $t_{1/2}/t_2$ (*) were 2.3–11 years for Σ_7 PCBs, 4.4–170 years for α -HCH, 4.1–30 years for γ -HCH, 2.1–4.6 years for endosulfan I, 1.6–6.7 years for endosulfan II, 5.0–27* years for endosulfan SO_4 , 3.3–14 years for dieldrin, 5.9–23* years for *cis*-chlordane, 15–7* years for *trans*-chlordane, 58–4.9* years for *trans*-nonachlor, 2.2–8.0 years for heptachlor, and 2.9–5.8 years for heptachlor epoxide (Table 1, Figure 3, Figures S10–S12).

The methods to identify global temporal trends for POPs are consistent within the data from the GAPS network, and trends can be compared between sites and POPs. The

challenges of comparing and assessing absolute temporal trend values from different monitoring campaigns have been discussed in depth by Kalina et al.⁴⁵ and Sharma et al.⁴⁶ Kalina et al. stressed the importance of 10+ year sampling periods for statistically significant temporal trends to compare to continuous active air sampling programs.⁴⁵ Sharma et al. highlights the important steps for interstudy time-trend reviews, i.e., QA/QC criteria, availability of raw data, and type of time trend analysis.⁴⁶ The criteria and recommendations in these studies are not all met here due to the nature of GAPS sampling and sample archiving. There is still a scarcity of temporal trend data for POPs in air, and application of a stringent filter as recommended by Sharma et al. will highly reduce the available data. Therefore, we focused on an overview of available data from literature (Table S1) and a general comparison to the temporal trends observed in our study. However, moving forward, a concerted effort should be made to enhance the comparability of the data acquired between different POP monitoring networks.

The decline rates for Σ_7 PCBs and the individual congeners are mostly consistent across this study (Figure 2, Figures S10, S13). Studies in the high Arctic⁴⁷ and the Great Lakes Basin^{48,49} report slower decline trends (and partially even increasing trends for PCBs) than those reported here. The temporal trends are in good agreement with data from Europe⁵⁰ and Africa.¹⁹ Kalina et al. reported temporal trends for individual PCBs from the MONET network for four of the sites monitored under the GAPS network, which agreed well.⁴⁵ Breivik et al. estimated the annual decrease in an emissions model for PCBs from old sources as $\sim 10\%$ for the mid-2000s, which would correspond with a halving time of ~ 6.5 years.⁵¹ This is in agreement with the halving time values from this

study and indicates that the concentrations of PCBs in air and their decline are still driven by primary sources.

The majority of sites showed decreasing concentrations of α - and γ -HCH in air (Figure 3, Figures S14, S15). α -HCH levels declined at a slower rate than γ -HCH. The first bans for the use of the technical HCH mixture and therefore the major source for α -HCH were implemented by many countries in the 1950s, much earlier than those for lindane in the 1980s.²⁹ The reemission of α -HCH from secondary sources might buffer the decline rates and lead to seemingly increased atmospheric halving times.⁵² For instance, Jantunen and Bidleman⁵³ reported that the reversal of air-sea gas exchange for HCHs in the arctic region, which was attributed to air concentrations declining faster than ocean water concentrations, resulting in a fugacity gradient favoring volatilisation. Increased melting of sea ice further enhances the outgassing effect.⁵³ This seems to be further confirmed by low or no decline for HCHs in air at the polar sites, reflecting the large reservoir of α - and γ -HCH in the Arctic Ocean. The halving times of α - and γ -HCH reported in this study are in agreement with values reported for the Arctic,⁴⁷ Great Lakes Area,^{48,49} the Tibetan Plateaus,⁵⁴ Europe,⁴⁵ and Africa¹⁹ (Table S1).

Endosulfan I levels declined at an overall higher rate than endosulfan II levels (Figure 3, Figures S16, S17), despite being the more stable of the two isomers. This can be explained by the overall higher levels of endosulfan I in the environment, which leads to more statistically robust data than the lower levels of endosulfan II. However, Endosulfan SO₄ levels were only declining at few sites and increasing at others, which reflects the persistence of the degradation product (Figure 3, Figure S18). Temporal trends for endosulfan SO₄ have only been reported for the Great Lakes area³⁹ and Africa.¹⁹ The temporal trends reported for Africa for endosulfan I/II and endosulfan SO₄ show the opposite trends with slower decline rates and increasing trends for the parent compounds and shorter halving times for the degradation product. This could be due to a different usage pattern across Africa that is not captured by the sole African long-term sampling site under the GAPS network. Overall halving times for endosulfan I/II were shorter than those reported in the Arctic but in agreement with values reported in the Great Lakes area⁴⁸ and Antarctica⁵⁵ (Table S1).

Dieldrin levels declined overall in this study (Figures S11, S19), though at low rates. Studies in Africa,¹⁹ Great Lakes Area,^{48,49} and the Arctic⁴⁷ show similar trends. Similarly, the temporal trends for *cis*-chlordane, *trans*-chlordane, and *trans*-nonachlor showed a combination of slow decline in most locations and increasing concentrations elsewhere across the sampling sites (Figure S12, Figures S20–S24). The reemission of legacy POPs from secondary sources might buffer the decline rates in the atmosphere. The increasing impact of secondary sources on the atmospheric levels of legacy POPs is difficult to identify in a 10 year passive air study. Longer-term measurements coupled with global fate modeling are needed to quantify the shift from a primary to secondary source controlled environment.⁵²

When comparing temporal trend slopes for GAPS 2005–2014 between compound groups with the Wilcoxon test, there are some significantly different groupings (Table S2). While there is obvious overlap in the temporal decline ranges for most compounds, the resulting trends for *trans*-chlordane and *trans*-nonachlor are significantly different from all other compounds except each other. On the basis of the common

source and similarities in degradation rates,⁵⁶ the expected grouping would include *trans*-chlordane, *trans*-nonachlor, and *cis*-chlordane (Figure S12). However, the temporal trends for *trans*-chlordane and *trans*-nonachlor are showing less declining tendencies than for *cis*-chlordane. On one hand, the lower levels of these compounds, which were often close to the MDL, led to statistically less robust data. On the other hand, the decline trends for compounds with lower levels in air could now be buffered by revolatilisation of these compounds from secondary sources, since restrictions on primary emissions have been in place in many countries for several decades. For these compounds, whose levels in air are now controlled by secondary emissions, first order decline kinetics is no longer a valid approach for describing temporal trends. It may be more appropriate to describe trends using a model that considers waning emissions from primary sources as well as contributions from secondary emissions and environmental degradation rates.^{3,52}

The temporal trends for endosulfan I were also considered statistically significantly different ($p < 0.05$) from those of most other compounds (Table S2). The range of temporal trends was skewed to steeper declining tendencies (Figure 3). The restrictions for endosulfan are more recent compared to those of the other compounds in this study. The steeper decline rates and shorter half-lives might reflect the effects of the recent restrictions of endosulfan. In addition to that, endosulfan has a lower environmental persistence score than the majority of compounds discussed in this study.⁵⁷

Principle component analysis (PCA) was applied to the temporal trend slopes at the individual sites ($n = 29$, sites with <50% detection frequency were excluded from the PCA) (Figure S25). The score graph shows that the scores for PC1 (51%) were mostly impacted by the diverging temporal trend patterns of endosulfan I/II and endosulfan SO₄/*trans*-chlordane/*trans*-nonachlor. The scores for PC2 (16%) were mostly impacted by the diverging temporal trend patterns of endosulfan I/II/SO₄ and *cis*-chlordane/*trans*-nonachlor. A closer look at the loadings assigned to the GAPS sites (Figure S25) did not show a clear grouping based on site type or regional group. However, any patterns might be obscured due to the vast majority of sites in the categories “Background” and “WEOG”.

The GAPS study has provided the most comprehensive view of global concentrations of persistent organic pollutants in the environment. The use of consistent sampling and analytical methods across more than 111 sites, 18 chemicals, and a wide variety of different ecosystems produced more than 18000 data points between 2005 and 2014 to reveal declining concentrations of legacy POPs around the world. Despite the success of the study and of the Stockholm Convention demands for discontinued use of these toxic compounds, major questions remain. There are still long-term data gaps for some regions (i.e., Russia, China). Data mining methods and global fate modeling are needed to identify the separation of secondary source emissions from legacy primary source stocks and from unreported new uses (i.e., production of PCBs as byproducts of paint production). Moving forward, a serious emphasis should be placed on enhancing the comparability of the data acquired between different POP monitoring networks to breach information gaps between regions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.1c01705>.

Figures, maps, and tables (PDF)

GAPS sites information, legacy POP concentrations for all samples and detection limits (XLSX)

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Notes

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REFERENCES

- (1) United Nations Environmental Program (UNEP) *Global monitoring report under the global monitoring plan for effectiveness evaluation*; Geneva, 2009.
- (2) United Nations Environmental Program (UNEP) *Stockholm Convention on Persistent Organic Pollutants (POPs), Text and Annexes*; <http://chm.pops.int/TheConvention/Overview/TextoftheConvention/tabid/2232/Default.aspx>, Revised 2017.
- (3) United Nations Environmental Program (UNEP) *Second global monitoring report under the global monitoring plan for effectiveness evaluation*; Geneva, 2017.
- (4) Herkert, N. J.; Martinez, A.; Hornbuckle, K. C. A Model Using Local Weather Data to Determine the Effective Sampling Volume for PCB Congeners Collected on Passive Air Samplers. *Environ. Sci. Technol.* **2016**, *50* (13), 6690–6697.
- (5) Herkert, N. J.; Spak, S. N.; Smith, A.; Schuster, J. K.; Harner, T.; Martinez, A.; Hornbuckle, K. C., Calibration and evaluation of PUF-PAS sampling rates across the Global Atmospheric Passive Sampling (GAPS) network *Environmental Science: Processes & Impacts* **2018**.20210
- (6) The University of Iowa PUF-PAS Sampling Rate Model Interface. http://s-iihr41.iihr.uiowa.edu/pufpas_model/ (January 2020).
- (7) Pozo, K.; Harner, T.; Lee, S. C.; Wania, F.; Muir, D. C.; Jones, K. C. Seasonally resolved concentrations of persistent organic pollutants in the global atmosphere from the first year of the GAPS study. *Environ. Sci. Technol.* **2009**, *43* (3), 796–803.
- (8) Pozo, K.; Harner, T.; Shoeib, M.; Urrutia, R.; Barra, R.; Parra, O.; Focardi, S. Passive-sampler derived air concentrations of persistent organic pollutants on a north-south transect in Chile. *Environ. Sci. Technol.* **2004**, *38* (24), 6529–6537.
- (9) Pozo, K.; Harner, T.; Wania, F.; Muir, D. C.; Jones, K. C.; Barrie, L. A. Toward a global network for persistent organic pollutants in air: results from the GAPS study. *Environ. Sci. Technol.* **2006**, *40* (16), 4867–4873.
- (10) Ruert, C.; Harner, T.; Schuster, J. K.; Eng, A.; Fillmann, G.; Castillo, L. E.; Fentanes, O.; Ibarra, M. V.; Miglioranza, K. S. B.; Rivadeneira, I. M.; Pozo, K.; Aristizábal Zuluaga, B. H. Air monitoring of new and legacy POPs in the Group of Latin America and Caribbean (GRULAC) region. *Environ. Pollut.* **2018**, *243*, 1252–1262.
- (11) Gouin, T.; Harner, T.; Blanchard, P.; Mackay, D. Passive and Active Air Samplers as Complementary Methods for Investigating Persistent Organic Pollutants in the Great Lakes Basin. *Environ. Sci. Technol.* **2005**, *39* (23), 9115–9122.
- (12) Ruert, C.; Harner, T.; Schuster, J. K.; Quinto, K.; Fillmann, G.; Castillo, L. E.; Fentanes, O.; Ibarra, M. V.; Miglioranza, K. S.; Rivadeneira, I. M. Towards a regional passive air sampling network and strategy for new POPs in the GRULAC region: Perspectives from the GAPS Network and first results for organophosphorus flame retardants. *Sci. Total Environ.* **2016**, *573*, 1294–1302.
- (13) Helsel, D. R. Fabricating data: how substituting values for nondetects can ruin results, and what can be done about it. *Chemosphere* **2006**, *65* (11), 2434–2439.
- (14) Anttila, P.; Brorström-Lundén, E.; Hansson, K.; Hakola, H.; Vestenius, M. Assessment of the spatial and temporal distribution of persistent organic pollutants (POPs) in the Nordic atmosphere. *Atmos. Environ.* **2016**, *140*, 22–33.
- (15) Meijer, S. N.; Sweetman, A. J.; Halsall, C. J.; Jones, K. C. Temporal Trends of Polycyclic Aromatic Hydrocarbons in the U.K. Atmosphere: 1991–2005. *Environ. Sci. Technol.* **2008**, *42* (9), 3213–3218.
- (16) Schuster, J. K.; Gioia, R.; Sweetman, A. J.; Jones, K. C. Temporal Trends and Controlling Factors for Polychlorinated Biphenyls in the UK Atmosphere (1991–2008). *Environ. Sci. Technol.* **2010**, *44* (21), 8068–8074.
- (17) Bloom, M. S.; Fujimoto, V. Y.; Storm, R.; Zhang, L.; Butts, C. D.; Sollohub, D.; Jansing, R. L. Persistent organic pollutants (POPs) in human follicular fluid and in vitro fertilization outcomes, a pilot study. *Reprod. Toxicol.* **2017**, *67*, 165–173.
- (18) Ekram Azim, M.; Letchumanan, M.; Abu Rayash, A.; Shimoda, Y.; Bhavsar, S. P.; Arhonditsis, G. B. Detection of temporal trends of α - and γ -chlordane in Lake Erie fish communities using dynamic linear modeling. *Ecotoxicol. Environ. Saf.* **2011**, *74* (5), 1107–1121.
- (19) White, K. B.; Kalina, J.; Scheringer, M.; Příbylová, P.; Kukučka, P.; Kohoutek, J.; Prokeš, R.; Klánová, J., Temporal Trends of Persistent Organic Pollutants across Africa after a Decade of MONET Passive Air Sampling *Environ. Sci. Technol.* **2020**. DOI: 10.1021/acs.est.0c03575
- (20) R Core Team R: A Language and Environment for Statistical Computing. <https://www.R-project.org/> (10/05/2020).
- (21) Wickham, H.; Francois, R.; Henry, L.; Müller, K. dplyr: A Grammar of Data Manipulation. R package version 1.0.2. <https://cran.r-project.org/web/packages/dplyr/index.html> (August 2020).
- (22) Carslaw, D.; Ropkins, K. CRAN Package ‘openair 2.7–6’. <https://cran.r-project.org/web/packages/openair/index.html> (October 2020).
- (23) Carslaw, D. C.; Ropkins, K. Openair—an R package for air quality data analysis. *Environmental Modelling & Software* **2012**, *27*, 52–61.
- (24) Stacklies, W.; Redestig, H.; Scholz, M.; Walther, D.; Selbig, J. pcaMethods—a bioconductor package providing PCA methods for incomplete data. *Bioinformatics* **2007**, *23* (9), 1164–1167.
- (25) Zhao, S.; Jones, K. C.; Li, J.; Sweetman, A. J.; Liu, X.; Xu, Y.; Wang, Y.; Lin, T.; Mao, S.; Li, K.; Tang, J.; Zhang, G. Evidence for Major Contributions of Unintentionally Produced PCBs in the Air of China: Implications for the National Source Inventory. *Environ. Sci. Technol.* **2020**, *54* (4), 2163–2171.
- (26) Bohlin-Nizzetto, P.; Melymuk, L.; White, K. B.; Kalina, J.; Madadi, V. O.; Adu-Kumi, S.; Prokeš, R.; Příbylová, P.; Klánová, J. Field- and model-based calibration of polyurethane foam passive air samplers in different climate regions highlights differences in sampler uptake performance. *Atmos. Environ.* **2020**, *238*, 117742.
- (27) Shoeib, M.; Harner, T. Characterization and comparison of three passive air samplers for persistent organic pollutants. *Environ. Sci. Technol.* **2002**, *36* (19), 4142–4151.
- (28) Erickson, M. D.; Kaley, R. G. Applications of polychlorinated biphenyls. *Environ. Sci. Pollut. Res.* **2011**, *18* (2), 135–151.
- (29) Vijgen, J.; Yi, L. F.; Forter, M.; Lal, R.; Weber, R. The legacy of lindane and technical HCH production. *Organohalogen Comp* **2006**, *68*, 899–904.
- (30) Li, Y.; Bidleman, T.; Barrie, L.; McConnell, L. Global hexachlorocyclohexane use trends and their impact on the arctic atmospheric environment. *Geophysical research letters* **1998**, *25* (1), 39–41.
- (31) Li, Y.; Zhulidov, A.; Robarts, R.; Korotova, L. Hexachlorocyclohexane use in the former Soviet Union. *Arch. Environ. Contam. Toxicol.* **2004**, *48* (1), 10–15.
- (32) Vijgen, J. *The Legacy of Lindane HCH Isomer Production: A Global Overview of Residue Management, Formulation and Disposal: Main Report*. International HCH & Pesticides Association: 2006.
- (33) Vijgen, J.; Abhilash, P.; Li, Y. F.; Lal, R.; Forter, M.; Torres, J.; Singh, N.; Yunus, M.; Tian, C.; Schäffer, A. Hexachlorocyclohexane (HCH) as new Stockholm Convention POPs—a global perspective on the management of Lindane and its waste isomers. *Environ. Sci. Pollut. Res.* **2011**, *18* (2), 152–162.
- (34) Li, Y. F.; Macdonald, R. W. Sources and pathways of selected organochlorine pesticides to the Arctic and the effect of pathway divergence on HCH trends in biota: a review. *Sci. Total Environ.* **2005**, *342* (1), 87–106.
- (35) Mackay, N.; Arnold, D.; Halsall, C.; Herbert, B.; Muir, D.; Small, J.; Solomon, K.; Weber, J., Evaluation and interpretation of environmental data on endosulfan in Arctic regions *Draft Report for Bayer CropScience Report Number CEA* **2005**, 107.
- (36) Weber, J.; Halsall, C. J.; Muir, D.; Teixeira, C.; Small, J.; Solomon, K.; Hermanson, M.; Hung, H.; Bidleman, T. Endosulfan, a global pesticide: a review of its fate in the environment and

occurrence in the Arctic. *Sci. Total Environ.* **2010**, *408* (15), 2966–2984.

(37) International Programme on Chemical Safety, Environmental Health Criteria 91, Aldrin and Dieldrin. 1989.

(38) Jorgenson, J. L. Aldrin and dieldrin: a review of research on their production, environmental deposition and fate, bioaccumulation, toxicology, and epidemiology in the United States. *Environ. Health Perspect.* **2001**, *109* (1), 113–139.

(39) Zitko, V., Chlorinated Pesticides: Aldrin, DDT, Endrin, Dieldrin, Mirex. In *Persistent Organic Pollutants*, Fiedler, H., Ed. Springer Berlin Heidelberg: Berlin, Heidelberg, 2003; pp 47–90.

(40) World Health Organization (WHO), Concise International Chemical Assessment Document 70, Heptachlor. Geneva, Switzerland. *World Health Organization Press. Available at* <http://www.inchem.org/documents/cicads/cicads/cicad70.htm> 2006.

(41) Buchert, H.; Class, T.; Ballschmiter, K. High resolution gas chromatography of technical chlordane with electron capture-and mass selective detection. *Fresenius' Z. Anal. Chem.* **1989**, *333* (3), 211–217.

(42) World Health Organization (WHO), IARC monographs on the evaluation of carcinogenic risks to humans. Volume 79: Some thyrotropic agents. *IARC monographs on the evaluation of carcinogenic risks to humans. Volume 79: Some thyrotropic agents.* **2001**.

(43) Bidleman, T.; Jantunen, L.; Wiberg, K.; Harner, T.; Brice, K.; Su, K.; Falconer, R.; Leone, A.; Aigner, E.; Parkhurst, W. Soil as a source of atmospheric heptachlor epoxide. *Environ. Sci. Technol.* **1998**, *32* (10), 1546–1548.

(44) Stockholm Convention GMP - Monitoring Reports. <http://chm.pops.int/implementation/globalmonitoringplan/monitoringreports/tabid/525/default.aspx> (2021–06–02).

(45) Kalina, J.; White, K. B.; Scheringer, M.; Příbylová, P.; Kukučka, P.; Audy, O.; Klánová, J. Comparability of long-term temporal trends of POPs from co-located active and passive air monitoring networks in Europe. *Environmental Science: Processes & Impacts* **2019**, *21* (7), 1132–1142.

(46) Sharma, B. M.; Kalina, J.; Whaley, P.; Scheringer, M. Towards guidelines for time-trend reviews examining temporal variability in human biomonitoring data of pollutants. *Environ. Int.* **2021**, *151*, 106437.

(47) Hung, H.; Katsoyiannis, A. A.; Brorström-Lundén, E.; Olafsdottir, K.; Aas, W.; Breivik, K.; Bohlin-Nizzetto, P.; Sigurdsson, A.; Hakola, H.; Bossi, R.; Skov, H.; Sverko, E.; Barresi, E.; Fellin, P.; Wilson, S. Temporal trends of Persistent Organic Pollutants (POPs) in arctic air: 20 years of monitoring under the Arctic Monitoring and Assessment Programme (AMAP). *Environ. Pollut.* **2016**, *217*, 52–61.

(48) Salamova, A.; Venier, M.; Hites, R. A. Revised Temporal Trends of Persistent Organic Pollutant Concentrations in Air around the Great Lakes. *Environ. Sci. Technol. Lett.* **2015**, *2* (2), 20–25.

(49) Shunthirasingham, C.; Gawor, A.; Hung, H.; Brice, K. A.; Su, K.; Alexandrou, N.; Dryfhout-Clark, H.; Backus, S.; Sverko, E.; Shin, C.; Park, R.; Noronha, R. Atmospheric concentrations and loadings of organochlorine pesticides and polychlorinated biphenyls in the Canadian Great Lakes Basin (GLB): Spatial and temporal analysis (1992–2012). *Environ. Pollut.* **2016**, *217*, 124–133.

(50) Graf, C.; Katsoyiannis, A.; Jones, K. C.; Sweetman, A. J. The TOMPs ambient air monitoring network – Continuous data on UK air quality for over 20 years. *Environ. Pollut.* **2016**, *217*, 42–51.

(51) Breivik, K.; Sweetman, A.; Pacyna, J. M.; Jones, K. C. Towards a global historical emission inventory for selected PCB congeners—a mass balance approach: 3. An update. *Sci. Total Environ.* **2007**, *377* (2–3), 296–307.

(52) Wöhrnschimmel, H.; MacLeod, M.; Hungerbühler, K. Global multimedia source-receptor relationships for persistent organic pollutants during use and after phase-out. *Atmos. Pollut. Res.* **2012**, *3* (4), 392–398.

(53) Jantunen, L. M.; Bidleman, T. F. Reversal of the Air-Water Gas Exchange Direction of Hexachlorocyclohexanes in the Bering and Chukchi Seas: 1993 versus 1988. *Environ. Sci. Technol.* **1995**, *29* (4), 1081–1089.

(54) Wang, C.; Wang, X.; Gong, P.; Yao, T. Long-term trends of atmospheric organochlorine pollutants and polycyclic aromatic hydrocarbons over the southeastern Tibetan Plateau. *Sci. Total Environ.* **2018**, *624*, 241–249.

(55) Hao, Y.; Li, Y.; Han, X.; Wang, T.; Yang, R.; Wang, P.; Xiao, K.; Li, W.; Lu, H.; Fu, J.; Wang, Y.; Shi, J.; Zhang, Q.; Jiang, G. Air monitoring of polychlorinated biphenyls, polybrominated diphenyl ethers and organochlorine pesticides in West Antarctica during 2011–2017: Concentrations, temporal trends and potential sources. *Environ. Pollut.* **2019**, *249*, 381–389.

(56) Yamada, S.; Naito, Y.; Funakawa, M.; Nakai, S.; Hosomi, M. Photodegradation fates of *cis*-chlordane, *trans*-chlordane, and heptachlor in ethanol. *Chemosphere* **2008**, *70* (9), 1669–1675.

(57) Rorije, E.; Verbruggen, E.; Hollander, A.; Traas, T.; Janssen, M., Identifying potential POP and PBT substances: Development of a new Persistence/Bioaccumulation-score **2011**.